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Synthesis and Characterization of Nanocrystalline CuO Embedded in Polymer

V. Shanmugam[1], M. Vishnudevan[2*], T. Seethalakshmi[3]

[1,3]Department of Physics, Government Arts College, Karur, TN, India.
*[*2]Department of Chemistry, Government Arts College, Karur, TN, India.*

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Abstract

Nanocomposite consists of Copper II oxide embedded in poly isopropanol has been synthesized by refluxing method using $CuCl_2$ as a precursor, $KMnO_4$ as an oxidising agent and isopropanol act as both solvent and polymer. The surface morphology of the nanocomposite were characterized by SEM and XRD. The optical properties were characterized by UV/Vis and PL studies and the dielectric properties of the nanocomposite material was calculated through capacitance and impedance values from AC impedance technique. The size of the synthesized nanocomposite was found to be in the range of 28 nm to 60 nm. The calculated energy gap from UV/Vis spectrum was 5eV which falls in the range of insulator. The calculated dielectric constant for CuO nanocomposite was found to be 21.47 and hence it may be used in gate dielectrics and passive components.

Keywords: *CuO; Impedance; Nanocomposite; Oxidizing agent.*

1. INTRODUCTION

Copper Oxide (CuO) generally has the characteristics of stable oxides of copper, but its nanocomposite has change in its physical, chemical and magnetic properties (Rehman *et al.* 2011). It has many spectrums of applications such as electro-optical properties, catalysis, sensors, solar cells and conducting film etc,. Mostly many researcher reported that the CuO nanoparticles as P-type semi conducting materials (Sanjay Srivastava *et al.* 2013; Jiji Koshy *et al*. 2015) with relatively small band gaps and show many attractive properties that can be used for variety of applications. Raja and Deepa (2015) and Nadaf *et al.* (2015) have synthesized and characterized polyaniline-copper oxide nano-composite materials by wet chemical and polymerization techniques and found that the synthesized polyaniline-copper oxide nano-composite exhibit unexpected properties that is lying in between semiconducting and conducting properties and XRD studies reveals that more crystalline nature of the composite materials.

There are many fabrication techniques reported (Sanjay Srivastava *et al*. 2013; Jiji Koshy *et al.* 2015; Pravanjan Malik, 2014; Kumar *et al.* 2001; Illy-Cherrey *et al.* 2002; Yu *et al*. 2007; Wijesundera, 2010; Wang *et al*. 2012) that are available for the preparation Copper II Oxide nanocomposite such as, Sol-gel, chemical precipitation methods, combustion method and refluxing method. Among these methods, refluxing method has been chosen for the present study of synthesis of CuO nanocomposite, because this method regulate constant energy in chemical reaction and it can regulate constant temperature on fixing suitable solvent for the synthesis of CuO nanocomposite. In this paper, we describe the synthesis of CuO nano-composite materials embedded in Poly-isopropanol by reflux method. The prepared samples and its electronic properties were characterized by UV/Vis, PL and Impedance spectrum and their size, shape and crystalinity properties were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and finally the existence of polymer was also confirmed by FTIR spectrum.

2. EXPERIMENTAL PROCEDURE

All the chemicals which are used in this experiment were of AR grade. The preparation of CuO composite nanoparticles were carried out using refluxing method (12) at 83 °C temperature and in this method 0.5 g of $CuCl_2$ mixed with excess of solvent

***M. Vishnudevan** **Tel. no: +919786817433**
Email: devan70@rediffmail.com

isopropanol (100 mL) and the mixer was heated at 83 °C and then $KMnO_4$ (0.94 g) solution was added slowly to the parent solutions. The mixture was carried out for 4 hrs in refluxing process, after 4 hrs refluxing we got a nanoparticles of black colour, that confirm the formation of Copper II oxides (CuO) and in presence large volume of solvent isopropanol it forms nanocomposite and the synthesized CuO nanocomposite was kept in microoven for 24 hrs. The sample was taken out from the oven and then air dried.

3. RESULTS & DISCUSSION

3.1 Electronic properties of CuO nanocompsite by UV/Vis Spectroscopy

The UV/Vis optical absorption spectrum of grown CuO nanostructures embedded in poly isopropanol was taken as shown in fig.1. In this the spectrum optical absorption was analysed to get the energy band gap of the material

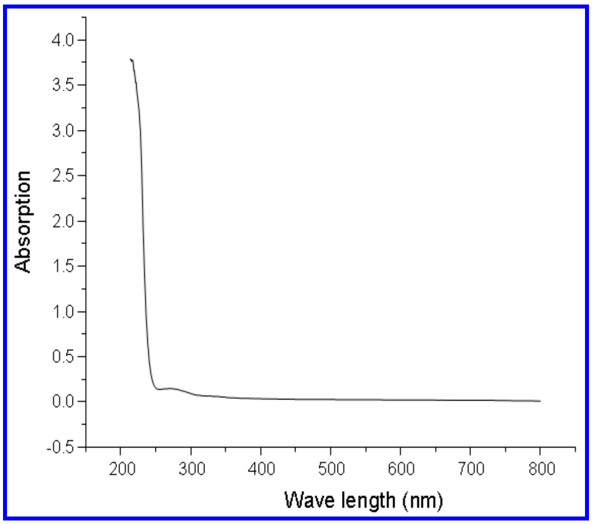

Fig. 1: UV/Vis absorption spectra of copper oxide nanocomposite synthesized by refluxing method

The material has a good optical absorption in the UV region and the cut off wavelength (λ_{cut}) is observed to be at 248nm which is more towards blue shift. The band gap energy (E_g) was calculated using the following well known equation.

$$E=hC/\lambda \text{ eV } (1 \text{ eV} = 1.602176565 \times 10^{-19} \text{J})$$

$$E_g=1240/\lambda \text{ eV}$$

where,

E_g- Bandgap energy (eV)

λ- Absorption wavelength (nm)

Band gap of copper oxide nanocomposite value was found to be 5eV. Thus ascertain that the nanocomposite was insulator.

3.2 Electronic properties of CuO nanocompsite by Photoluminescense Spectroscopy

The photoluminescence spectrum display emission band with a maximum 362.92nm and a shoulder at 522.69 nm (as shown in fig.2), which could arise from inhomogeneous size of copper oxide nanocomposite. The copper oxide exhibit a strong emission peak in the near UV region and a broad band in the visible region. The strong peak seen at 362.92nm corresponding to the near band edge (NBE). The intensity of the NBE emission of CuO nanoparticle is dependent on the nano crystalline structure.

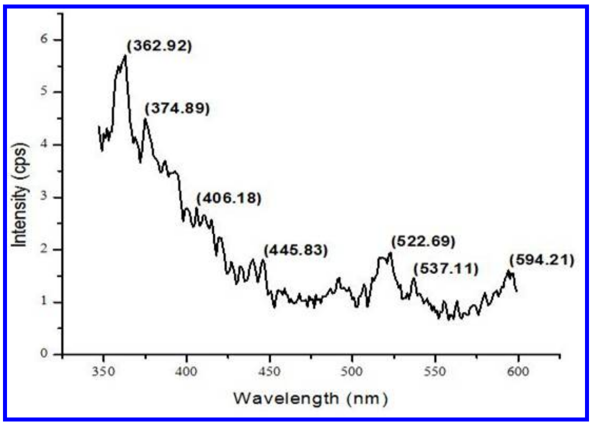

Fig. 2: Photoluminescence spectra of copper oxide nanocomposite synthesized by refluxing method

3.3 Functional group Characterization of CuO nanocomposite by FTIR study

The spectrum of CuO nanocomposite powdered specimen was taken in the range of 400-4000 cm^{-1} wave length as shown in fig.3. For the peaks in the range of 580-990 cm^{-1} are attributed to the C-H bending vibration of –HC-CH- bond. The two absorption peaks that appear at 1730 and 1135 cm^{-1} are due to the O-H bending and C-O stretching.

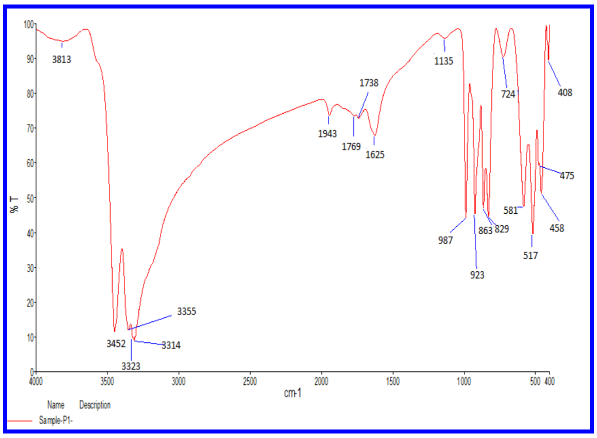

Fig. 3: FTIR spectra of copper oxide nanocomposite synthesized by refluxing method.

The bands observed at 3452 cm^{-1} are characteristics of O-H stretching vibrations. The peak in the range 724-860 cm^{-1} is attributed to the C-H bending vibration of the –HC-CH- bond. This study confirm existence of the polymer isopropanol along with grown CuO nanoparticles.

3.4 Dielectric properties of CuO nanocomposite by AC-Impedance study

The dielectric properties of CuO nanocomposite was calculated by Impedance Spectroscopy (of Model VERSA STAT MC) with the frequency range of 1 Hz to 1MHz. The study of impedance spectrum of CuO nanocomposite as shown in the fig.4 Nyquist plot. From the plot the impedance value, capacitance value and dielectric properties of the nanocomposite were calculated. The impedance spectra of CuO nanocomposite exhibited semicircle indicate that the electrical conductivity value was very low compared with bulk and nanomaterial of CuO.

Dielectric properties was calculated from AC-Impedance spectrum by substituting the calculated values of capacitance (0.1106 nF) and impedance (10k.Ohms) in the following equation:

$$C= \varepsilon_0 \varepsilon_r A/d$$

where C= Capacitance

A = Area of the sample

d = dimeter of the sample

ε_0 = permittivity of the vacuum

ε_r = Dielectric constant

Dielectric constant = 21.

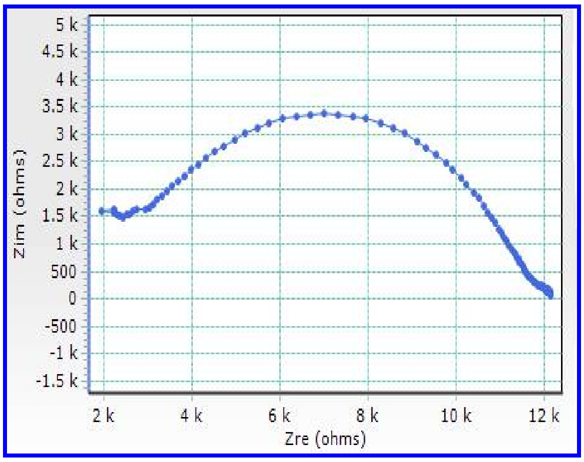

Fig. 4: Nyquist plot of copper oxide nanocomposite synthesized by refluxing method.

3.5 Characterization of surface morphology by SEM

Surface morphological characteristics such as particle size, shape has been characterized by Scanning Electron Microscopy (SEM) (Model ZEISS). The SEM image of CuO embedded in polymer isopropanol was shown in fig 5. From the SEM image it was observed that the synthesized CuO composite nanoparticles were in crystal form. The morphology of the prepared CuO nanoparticles in polymer composite is looks like pollen grain with a non uniform size of 28 nm to 60 nm.

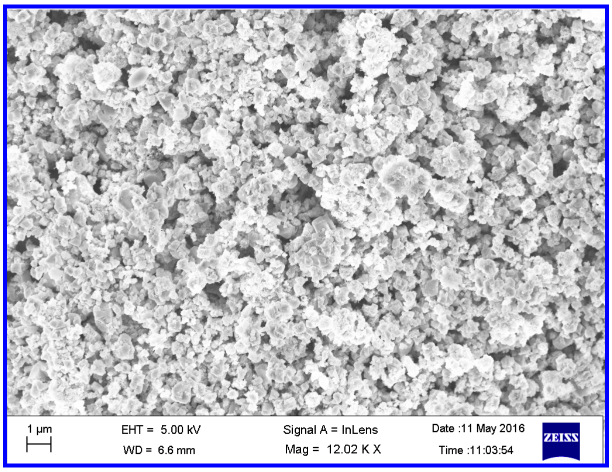

Fig. 5: SEM image of CuO Composite nanoparticles with polymer isopropanol

3.6 Characterization of surface morphology by XRD

X-ray diffraction study of copper oxide nanocomposite synthesized by refluxing method was observed to be in purely crystalline in nature and it was shown in fig.6. Average particle size of copper oxide nanoparticle was found to be in the range of 28.41nm.

The XRD spectra showing the intense peak at 28.41˚ is having plane (020) which is the crystal plane of CuO. The low intensity peak at 16.27˚, 32.41˚, 39.82˚, 40.5˚, 50.29˚ and 53.69˚which match well with the plane (001), (02-1), (11-1), (111), (003) and (130) indicates that the prepared CuO composite is highly crystallines characteristic of pure monoclinic crystals and well arrange in specific orientation. The size of the copper crystals were estimated from the Debye-Scherer equation.

$$D=K\lambda COS\theta/\beta$$

Where, K is the Scherer constant, which is related to the crystallite shape and are the radiation wavelength and Bragg's angle, respectively and is the full width at half maximum of the diffraction peak. The crystal size of the products as calculated by Scherer formula was 28.41nm.

Grain size calculation

The average grain size is calculated from the Scherer's formula,

$$D=0.9\cos\theta/\beta$$

where,

λ is the wavelength of copper k line (1.54056Å)

θ is the diffraction angle

β is the full width at half maximum of the peak

D is the average particle size

Dislocation density

The dislocation density was calculated from the grain size using the following equation:

$$\delta = 1/D^2$$

Strain

The strain was calculated by the formula,

$$\varepsilon=\beta\cos\theta/4$$

Where,

β is the half width full maximum

Inter Planar Spacing (hkl)

The inter planar spacing (hkl) was calculated using the formula,

$$1/d^2=h^2/a^2\sin^2\gamma+k^2/b^2\sin^2\gamma-2hk\cos\gamma/ab\sin^2\gamma+l^2/c^2$$

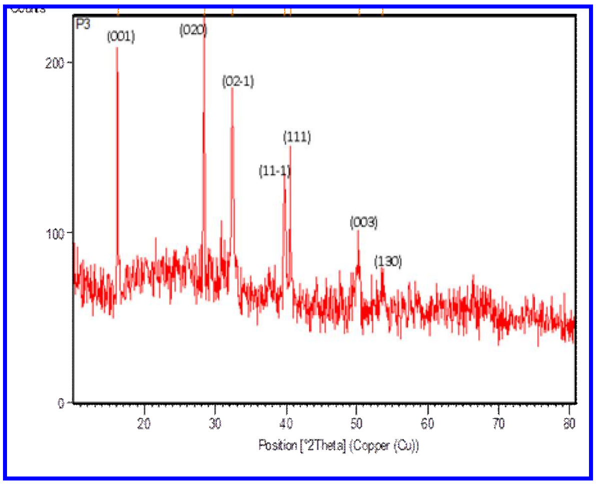

Fig. 6: Powder XRD Spectra of CuO nanocomposite

Table 1. Characterization of surface morphology

Material	Grain size (nm)	Dislocation Density Kg/m^3	Micro strain
CuO	28.41	0.00349	0.075511

4. CONCLUSION

Copper II Oxide nanomaterials embedded in Polyisopropanol has been synthesized by refluxing method. The electronic properties of this nanocomposite by UV/Vis and PL studies confirmed that it has large band Gap value of 5 eV. The FTIR spectrum reveals that the existence of polymer (poly-isopropanol) on the CuO-Polymer composite matrix. The XRD studies characterizes the crystalline nature of CuO nanocomposite. The SEM study observed that the size of the grown CuO in the polymer has non uniform size in the range of 28nm-60 nm. The AC-Impedance study confirmed the composite material has dielectric property and the calculated dielectric constant was 21. From these above studies conducted it was concluded that the CuO-polymer nanocomposite possess crystalline nature along with dielectric properties.

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